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# Grafting of Oligomers on Phenolic Polymer Chains and Its Influence on Their Titration Curves in Nonaqueous Media

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## ABSTRACT

A linear phenolic polymer has been prepared by condensing p-bromophenol with formaldehyde in the presence of a catalyst. The linear polymer was dehalogenated completely by a standard procedure. Some oligomers of uniform structure and molecular weight were grafted on the dehalogenated polymer. Electrometric titration curves of the grafted copolymers have been studied, and the shape of the titration curves has been interpreted in terms of the length of the grafted chain and the intramolecular H-bonding between neighbouring OH groups.

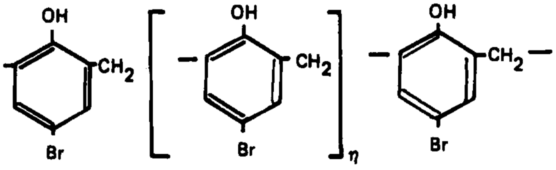
## INTRODUCTION

Graft copolymers can be prepared either by polymerization of a second monomer onto an existing polymer chain or by combining preformed polymer chains with other polymer chains with the aid of functional groups. It is well known that the length, chemical nature, and concentration of the side chains influence the overall properties of graft copolymers [1]. Some preliminary work from this laboratory indicated that it is possible to graft small chains on phenolic copolymers [2]. For the present study efforts have been made to graft oligomers of known structure and uniform molecular weight on phenolic polymer chains. Since the chemical nature of the side chains are identical with the main chain and the length of the side chains is also known from its synthesis, only the concentration of side chains may influence the ultimate properties of the graft copolymer. Phenolic polymers and oligomers are known to exhibit peculiar properties which have been attributed to the presence of intramolecular H-bonding between neighboring OH groups [3-7]. Moreover, the dissociation behavior of linear phenolic polymer chains in nonaqueous solvents has been reasonably established [6-8]. The main aim of this investigation was to establish the grafting on model phenolic polymer chains and its likely influence, particularly on the dissociation behavior of copolymers in nonaqueous media.

## EXPERIMENTAL

### Preparation of Copolymer

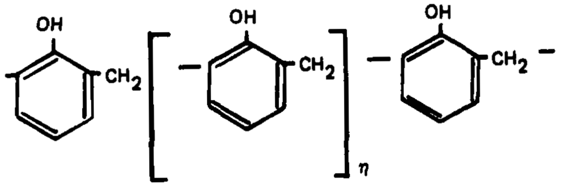
The copolymer, p-bromophenol-formaldehyde (I), was prepared by refluxing the components in a definite molecular proportion in the presence of 2 mL of 10 N HCl, used as catalyst, for 2½ h.



I

### Dehalogenation of Copolymer

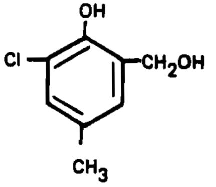
The complete dehalogenation of Copolymer I was effected by refluxing it with an excess of metallic sodium in monoethanolamine-dioxane mixture for ½ h at 120°C, and neutralizing the reaction product with 5% acetic acid. The dehalogenated copolymer II thus obtained was filtered, washed, and dried [2].



II

## Preparation of Substituted Monomers and Oligomers

The monomer III and oligomers IV and V were prepared from p-cresol using the methods of Sah-Anderson [9] and Kämmerer-Rasauch [10].



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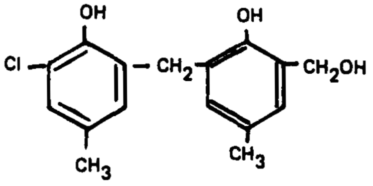

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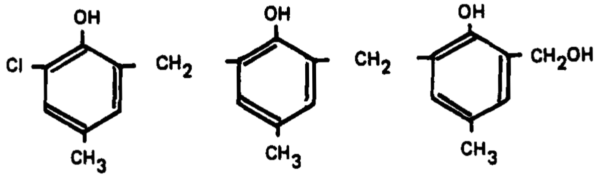


V

## Grafting on the Main Chain

The dehalogenated Copolymer II was mixed with a 10% excess of the stoichiometric quantities of Components III, IV, or V, respectively, dissolved in an acetone-methanol mixture, and refluxed in the presence of 10 N HCl as catalyst for 2 h. The resultant product was poured in cold water, filtered, and washed several times with water and methanol to remove HCl and the unreacted components (e.g., III, IV, or V).

## Conductometric Titrations

The conductometric titrations were carried out using a Leeds-Northrup conductivity bridge (4959).

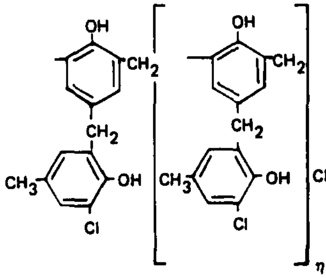
## Potentiometric Titrations

For potentiometric titrations a Radiometer pH meter (Model pHM 26 C) with a glass electrode (G 202 B) and a calomel (K 401) reference electrode was used.

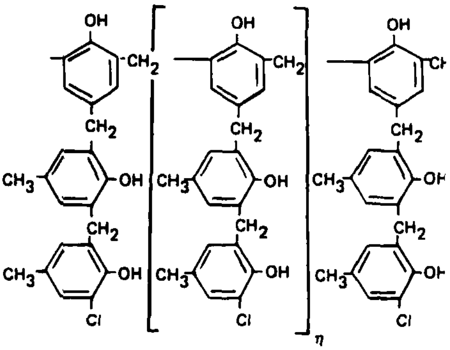
For conductometric and potentiometric titrations, acetone was used as the medium and sodium methoxide as the titrant base. The details of the titration procedure have been described elsewhere [6].

## RESULTS AND DISCUSSION

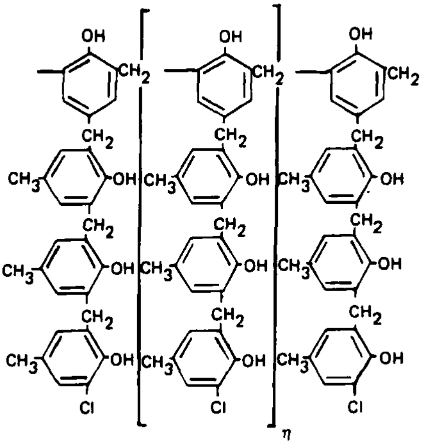
p-Bromophenol-formaldehyde Copolymer I has been characterized by electrometric titrations techniques in nonaqueous media [6], and its number-average degree of polymerization (DP) has been found to be around 12. Copolymer I was then completely dehalogenated and its DP has been checked once again to see whether degradation has taken place or not. The DP of the dehalogenated product was found to be unchanged. Since all the para positions of the dehalogenated product are active, therefore, hydroxymethyl derivatives of phenolic monomers and oligomers (e.g., III, IV, and V) on these positions could be attached under suitable experimental conditions. On the assumption that if all the para positions of Copolymer II are attached with the respective monomer or oligomer (i.e., III, IV, or V) units, then the probable structure of the grafted copolymers can be written as follows:



VI



VII



VIII

One can calculate the total amount of acidic functional groups in milliequivalents per 100 g of copolymer from these structures (e.g., VI to VIII). Since Copolymer I or the corresponding dehalogenated product II contains on an average 12 repeating units, the total number of phenolic units (i.e., including the side chains) in Copolymers VI, VII, and VIII should be 24, 36, and 48, respectively. Of course, this is on the assumption that each para position of the dehalogenated product is attached with the respective monomer or oligomer unit. By dividing the total amount of base required to neutralize all the OH groups per 100 g of the copolymer by the total number of phenolic units (e.g., 24, 36, or 48) in the grafted copolymers, one can obtain the contribution of each monomeric unit. For instance, in the case of Copolymer VI the amount of base required for neutralizing each phenolic unit should be 789/24 = 32 (789 being the calculated amount of base required to neutralize all the OH groups per 100 g of Copolymer VI. Similarly, the calculated amount of base for each phenolic unit for Copolymers VII and VIII is 22 and 17 milliequivalents per 100 g of copolymer, respectively.

Figures 1 to 3 show the potentiometric and conductometric titration curves of graft copolymers VI and VII. The conductometric curves of all the copolymers (e.g., Curve A of Figs. 1 to 3) showed several distinct breaks before complete neutralization of all the OH groups in a given weight of copolymer. However, the corresponding potentiometric curves indicated only one or two sharp inflections. As can be seen from Figs. 1 to 3, the nature of the titration curves changes with the length of the side chain (i.e., III, IV, or V). Interestingly enough, the breaks in the conductometric curve for Copolymer VI to VIII occur in multiples of 32, 22, and 17 milliequivalents, respectively (cf. Curve A of Figs. 1 to 3). The coincidence of calculated and ex-

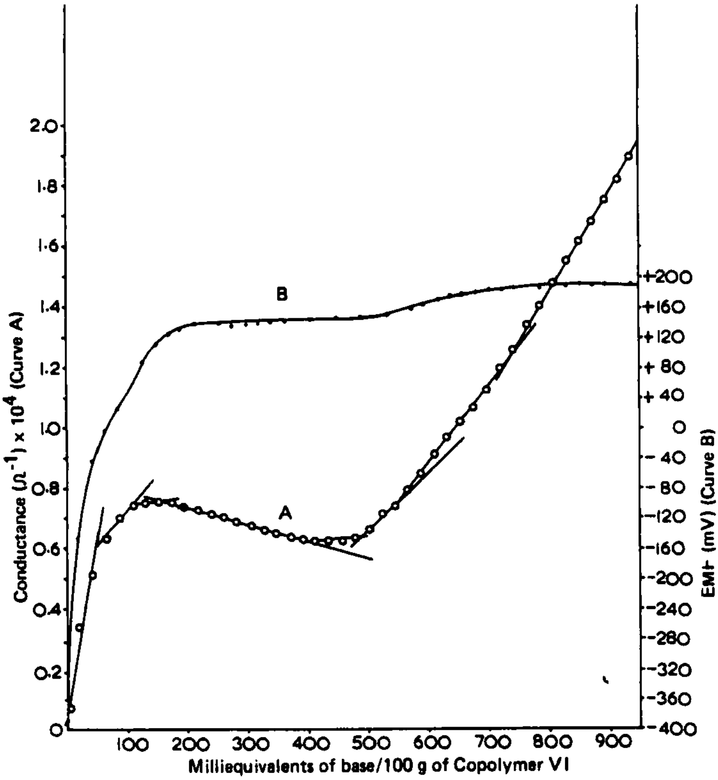
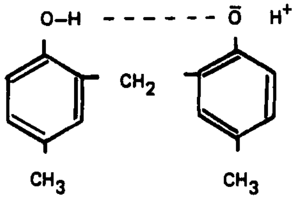


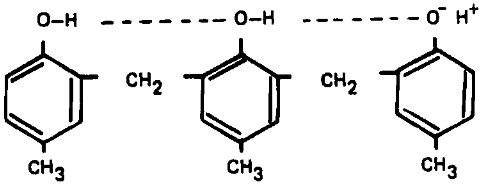
FIG. 1. Titration curves of Copolymer VI. Conductometric curve: (A) in acetone with sodium methoxide. Potentiometric curve: (B) in acetone with sodium methoxide.

perimentally observed values probably indicates that grafting of oligomers has taken place quantitatively.

One can possibly interpret the pattern of neutralization of OH groups in the grafted copolymers VI to VIII by comparing the conductometric titration curves of the two oligomers (IX and X) which are shown in



IX



X

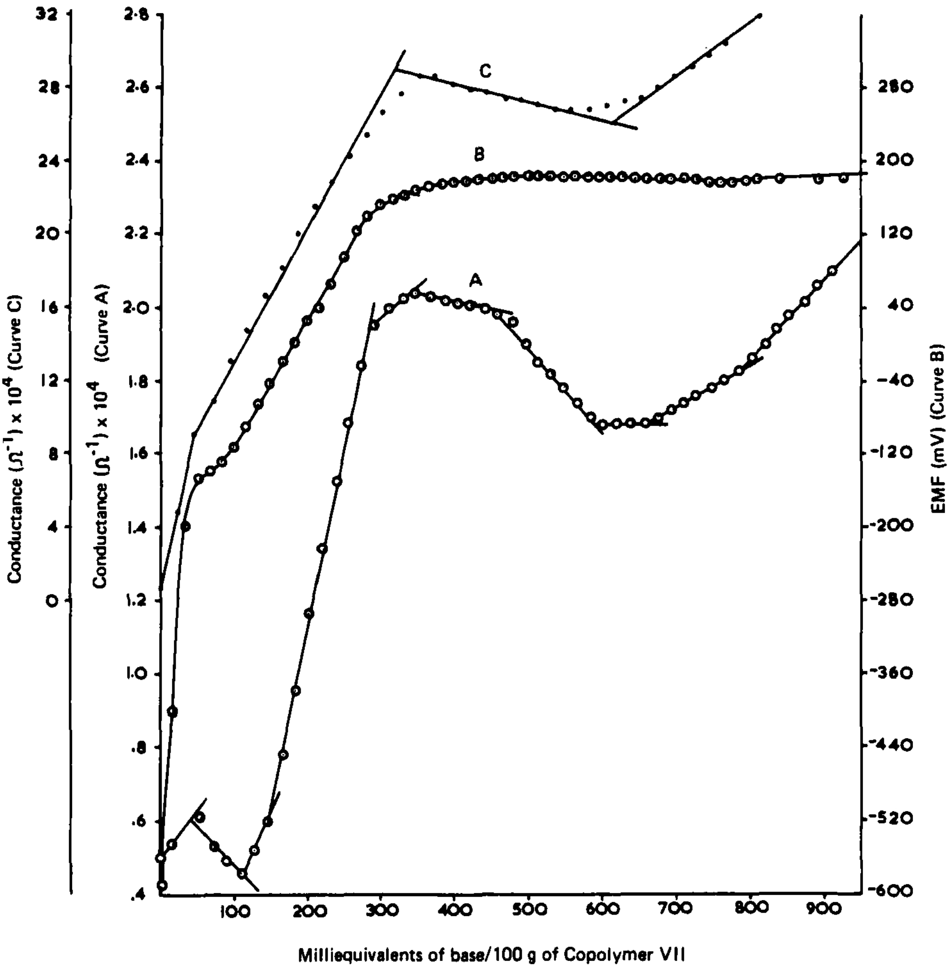


FIG. 2. Conductometric titration curves in acetone with sodium methoxide: (A) Copolymer VII; (C) dinuclear oligomer IV. (B) Potentiometric curve of copolymer VII in acetone with sodium methoxide.

Fig. 2 (Curve C) and Fig. 3 (Curve C), respectively. It is well known that oligomers have hyperacidic hydroxyl groups as a result of intramolecular H-bonding, and the neutralization of their hydroxyl groups takes place in distinct steps [3, 11]. The neutralization of the second hydroxyl group (weaker) in oligomers is accompanied by a sharp fall in conductance (cf. Curve B of Figs. 2 and 3). If this feature is compared with the conductometric titration curve (i.e., Curve A of Fig. 2)

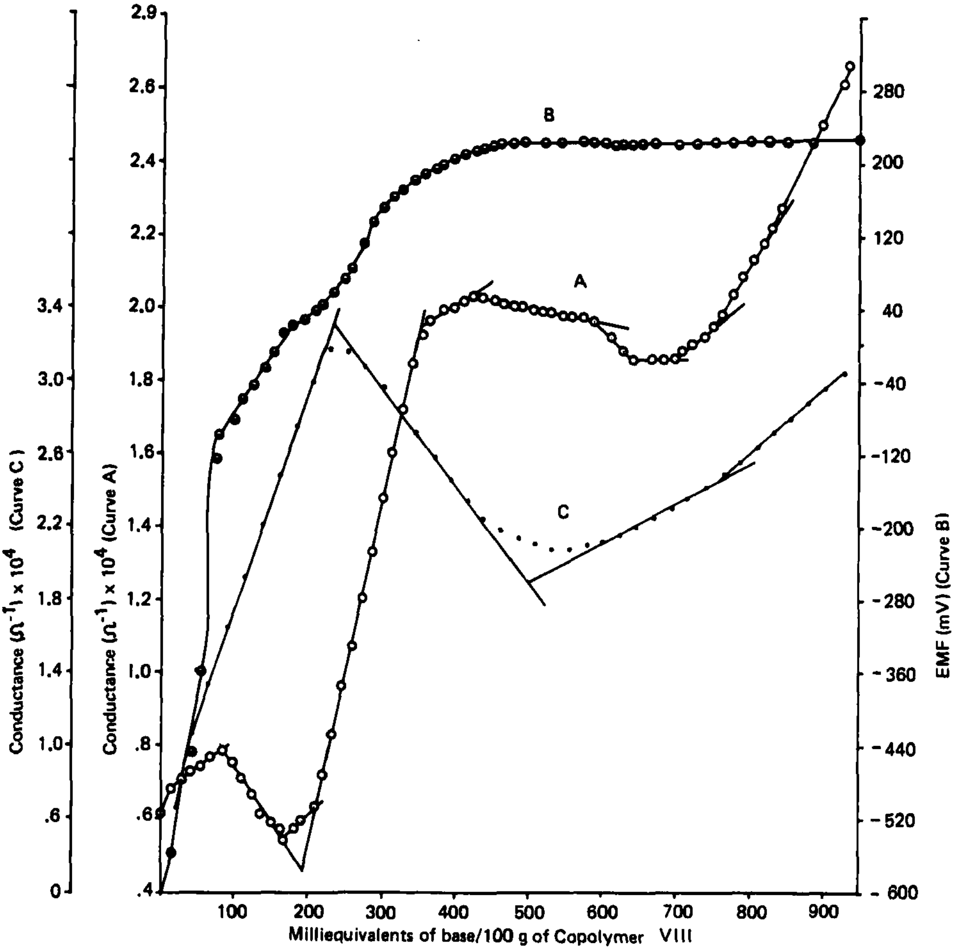


FIG. 3. Conductometric titration curves in acetone with sodium methoxide: (A) Copolymer VIII; (C) trinuclear oligomer V. (B) Potentiometric curve of Copolymer VIII in acetone with sodium methoxide.

of the dinuclear grafted Copolymer VII, it is observed that the final fall in conductance occurred up to 590 milliequivalents of base per 100 g of copolymer. However, the calculated amount of base required for neutralizing all the side chains (e.g., dinuclear chains) for this copolymer (i.e., VII) is 24 × 22 = 528 milliequivalents. Since one cannot rule out the possibility of the presence of hydrogen-bonded hydroxyls (i.e., hyperacid hydroxyls) in the main chain as well, the slight ex-

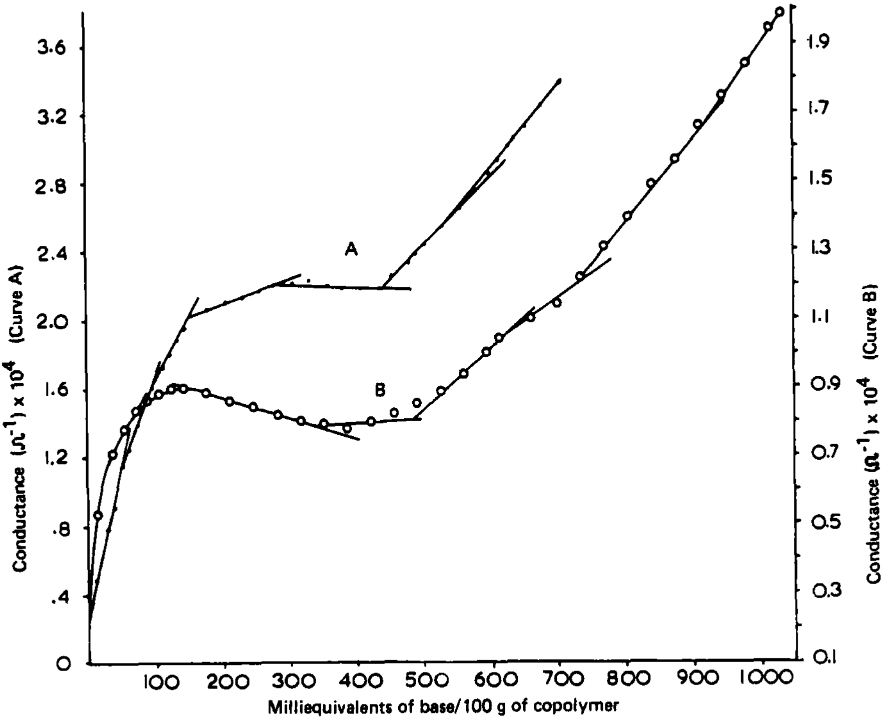


FIG. 4. Conductometric titration curves in acetone with sodium methoxide. (A) Copolymer I; (B) dehalogenated Copolymer II.

cess value at the final fall in conductance in the titration curve can be accounted for. On the basis of similar arguments, the neutralization of OH groups of the side chains and their influence on the nature of the titration curves of the other graft copolymers (VI and VIII) can also be accounted for. The validity of this argument can be checked further by comparing the conductometric titration curves of linear phenolic polymers (I and II) with those of the graft copolymer (VI to VIII) (compare Curves A and B of Fig. 4 with Curve A of Figs. 1 to 3).

An important difference between conductometric and potentiometric titration curves is the presence of a large number of distinct breaks in the former compared to a very small number of inflections in the latter. One can expect such a discrepancy in view of the fact that factors such as ion association, low dielectric constant of the medium, and acid-anion complex formation will influence the conductometric titration curve much more than the potentiometric curve. Moreover, the difference in the degree of dissociation of the various acid-anion complexes which might have been formed in a medium of low dielectric constant could probably be responsible for the neutralization of acidic groups in distinct steps in the conductometric curve. In the case of weak acids, such a homoconjugation has also been observed by Kolthoff and co-workers [12].

Thus it may be concluded that dehalogenation of linear phenolic copolymer gives rise to reactive positions, where suitable monomers or oligomers can be grafted. The length of the oligomer side chains greatly influences the shape of the titration curves in nonaqueous media.

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